

A SPECTROPHOTOMETRIC STUDY OF THE
GOLD(III)-5-(p-ETHOXYANILINO)-5,6-DIHYDROURACIL CHELATE

by *DEM*

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INTRODUCTION

Although used for many years in analytical chemistry, chelates have not been understood or studied extensively until very recently. The Egyptians first used them, unknowingly, when they tested wine for iron, one of the most common impurities found in wine, by adding crushed tree galls to the wine. A bright red color proved that iron was present.

A chelate is formed by the combination of a metal ion with a substance which contains two or more electron donor groups. It is a special case of complex or coordination compound, that is, a compound formed by the union of a metal ion with an electron donor. The name given to the substance which contains the electron donors is "ligand." The bonds between the metal ion and the ligand may be "essentially ionic" or "essentially covalent" in nature. The type of bond is determined by the nature of the metal and the donor atoms, according to Martell and Calvin (6) p. 1.

Chelates are of increasing importance in theoretical and applied chemistry. In analytical chemistry they provide a means for rapid determination of substances and also a convenient method of rendering interfering ions in a form in which they no longer interfere. They have also been found valuable in softening water, recovering trace amounts of materials from factory wastes, and in other applications where it is desired to remove small amounts of substances from solution or to prevent them from reacting.

The chemical and physical properties of chelates are generally quite different from either the metal ion or the ligand. Quite frequently an aspect of these changes is a marked change in color, as is true in the case studied here. Because of this property, spectrophotometry is frequently a reliable method for the study of chelate compounds.

This thesis presents a spectrophotometric study of the chelate formed by the gold (III) ion and 5-(p-ethoxyanilino)-5,6-dihydrouacil. Gold (III) was chosen because of a lack of analytical methods for this species and also because the reaction between gold (III) and the ligand appeared to produce a deep color which would be excellent for spectrophotometric study. The research fell naturally into four distinct parts. First, the optimum pH value for chelate formation was determined, as was the optimum wavelength for further study of the system. Second, the molecular ratio of metal to ligand was determined by a continuous variation study. Third, the range of metal ion concentration for which the chelate was analytically useful was determined. Finally, extraction studies were conducted with various organic solvents.

REVIEW OF LITERATURE

The phenomenon of complex compounds, although observed and utilized from ancient times, was first explained theoretically by Werner (10). However, there were apparent conflicts created by Werner's theory. It created a false distinction between

organic and inorganic compounds and postulated primary and secondary valences with no theoretical justification, according to Martell and Calvin (6), p. 7. These conflicts were resolved by Sidgwick (8) in his electronic theory of valence and complex formation. This theory reconciled electrovalence and covalence and introduced a new concept, coordinate covalence.

Formation of coordination complexes can also be explained in terms of Lewis' electronic theory of acids and bases (5). This theory considers all acids to be electron acceptors and all bases to be electron donors. Thus the reaction between an acid and a base is simply the formation of a coordinate bond under this theory. As defined in the introduction, therefore, all metals are "acids" when they form complexes and all donor groups or ligands are "bases."

The study of chelates as a group distinct from complex compounds in general may be said to have originated with the coining of the word chelate by Morgan and Drew (7). They derived it from the Greek word for the claws of lobsters and other crustaceans, "chela." It is rather appropriate as the donor groups in chelating agents or ligands are in such a position that they "close" with the central metal ion to form a heterocyclic ring, usually containing five or six atoms.

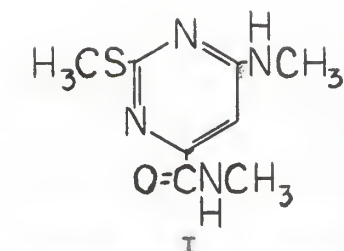
Research on this group of compounds has accelerated greatly since 1920 as new uses for these compounds have been found. Bjerrum's (1) development of a titrimetric method for determining the stability constants of chelates and, from these, thermo-

dynamic values has lent great impetus to further study of these compounds and placed them on an even firmer theoretical basis. At the present time much of the work being done with these compounds is directed toward obtaining chelates which are specific for particular metals and which are specifically suited for a particular function.

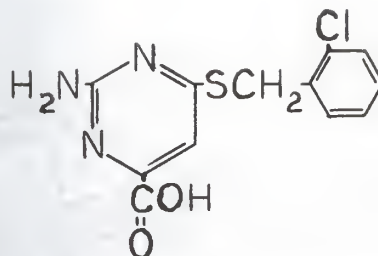
PRELIMINARY STUDIES

Four prospective ligands were investigated to discover if they form chelates. Color production was used as a test for chelate formation. Hundredth molar solutions of each of these ligands were produced by dissolving them in 500 ml. of an appropriate solvent. The solvents were ethanol for ligand I, pyridine for ligand II, and water plus 10.00 ml. of concentrated sodium hydroxide in 500 ml. of solution for ligands III and IV. They were then tested with hundredth molar samples of fifty-eight different metal ions. The tests were conducted by mixing 1.00 ml. of the hundredth molar metal with 5.00 ml. of the hundredth molar ligand solution, diluting to about 30 ml. with distilled water, adjusting the pH slowly from 1.00 to 12.00 while stirring the solution vigorously with a magnetic stirrer, and observing the visible changes, if any, which occurred over this pH range.

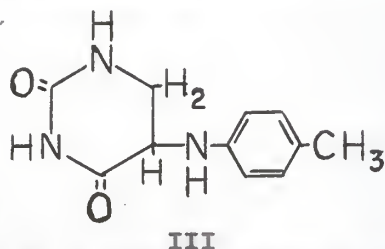
The structural formulas of the possible ligands which were studied are shown in Figure 1.



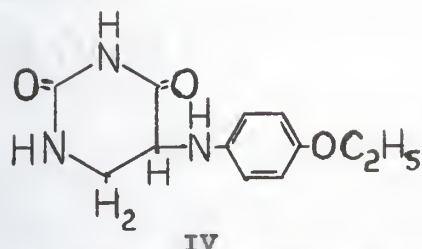
6-methylamino-2-methylthio-4-pyrimidino-N-methyl carboxamide



2-amino-4-carboxyl-6-(o-chlorothiobenzyl) pyrimidine



5-(p-methylanilino)-2,4-dioxo-5,6-dihydropyrimidine



5-(p-ethoxyanilino)-5,6-dihydrouracil

Figure 1. Structural formulas of the prospective ligands studied.

The names of these prospective ligands are (I) 6-methylamino-2-methylthio-4-pyrimidino-N-methyl carboxamide, (II) 2-amino-4-carboxyl-6-(o-chlorothiobenzyl) pyrimidine, (III) 5-(p-methylanilino)-2,4-dioxo-5,6-dihydropyrimidine, and (IV) 5-(p-ethoxyanilino)-5,6-dihydrouracil.

Of the fifty-eight metal ions examined, the following did not react visibly with any of the ligands: As(III), As(V), Be(II), Bi(III), Ca(II), Ce(III), Li(I), Mg(II), K(I), Rb(I), Se(IV), Se(VI), Si(IV), Na(I), Te(IV) (TeO_2 in NaOH), Te(VI),

Tl(I), and W(VI).

The results of the preliminary investigations on the other metal ions tested are summarized in Table 1. The notation "no change" which appears in the table indicates that the metal reacted in the same manner with or without the ligand, that is, the ligand produced no apparent change in the reaction of the metal. The numbers in the table refer to pH values and all colors are for solutions unless it is stated that a precipitate is present. The notation "no ppt. at any pH" means that although the metal precipitated when alone, it did not precipitate in the presence of the ligand being tested.

The masking effect of the ligands, evidenced by lack of precipitation for metal ions which would normally have precipitated, could be quite useful when these ions might interfere with a desired reaction.

The final choice of a system for intensive study involved the screening of several metal-ligand systems. Criteria for choosing the system to be studied were: (1) intensity of color, (2) presence of only one color, (3) lack of precipitation, and (4) lack of side reactions. The color intensity was important as it was desirable to find a system sensitive to small concentrations of the metal ion. Also, more accuracy is possible with a high extinction coefficient for the system. One color would indicate that only one compound was formed. Precipitation was obviously undesirable in a spectrophotometric study, and side reactions, such as oxidation and reduction, would tend to produce

Table 1. Summary of preliminary studies

Metal Ion	Ligand				
	:	:	:	:	:
	I	II	III	IV	:
Al(III)	No Change ¹	White ppt. 5.50-8.00 ²	No Change	No Change	
Sb(V)	No Change	White ppt. 1.00-4.90	No ppt. at any pH	1.00-4.00 cloudy pink ³ 4.00-7.00 light orange	
Ba(II)	No ppt. at any pH	White ppt. 5.50-12.00	No Change	No Change	
Cd(II)	White ppt. at 12.00	No Change	No Change	No Change	
Ce(IV)	No Change	No Change	2.00-6.00 pink 6.00-8.00 tan ppt. 8.00-12.00 light tan	1.00-7.00 clear purple 8.00-12.00 orange	
Cr(VI)	No Change	No Change	No Change	1.00-5.00 brown to orange	
Co(II)	No Change	5.50-12.00 White ppt.	No ppt. at any pH	1.00-5.00 light purple 5.00-7.00 purple-orange 7.00-12.00 orange	
Co(II) & Co(III) (Co ₃ O ₄)	2.00-8.00 faint pink 8.00-12.00 green blue	1.00-12.00 dirty white ppt.	1.00-2.00 very faint pink 5.00-7.00 yellow ppt. 7.00-12.00 yellow	1.00-4.00 light purple 4.00-12.00 light yellow; slight yellow ppt.	

Table 1. (Cont.)

Metal Ion	Ligand			
	I	II	III	IV
Cu(I)	7.00-8.00 light green 9.00-12.00 slight green ppt.	5.50-12.00 cloudy blue- green	2.00-6.90 slight green ppt. 7.00-9.00 green 9.00-12.00 light blue	5.90-9.00 green ppt. 9.00-12.00 green
Cu(II)	No Change	5.50-12.00 blue-green ppt.	2.00-4.79 slight green ppt; dark green 4.79-9.00 light green 9.00-12.00 light blue	1.00-6.00 green ppt. 6.00-12.00 light green
Au(III)	No Change	No Change	1.00-11.51 purple-black 11.51-12.00 light tan	1.00-7.00 deep-purple- black 7.00-11.00 black 11.00-12.00 brown-black
In(III)	No ppt. at any pH	5.50-9.00 slight white ppt.	No ppt. at any pH	No ppt. at any pH
Ir(IV)	1.00-5.00 yellow- brown	No ppt. at any pH	1.00-7.00 light orange 7.00-12.00 light yellow	1.00-4.00 slight orange 4.00-6.50 slight purple
Fe(II)	No Change	5.50-12.00 reddish- brown	1.00-12.00 slight yellow ppt.	1.00-8.00 yellow; slight brown ppt. 8.00-12.00 clear golden
Fe(III)	No Change	1.00-12.00 yellow; lighter at higher pH	1.00-12.00 slight yellow ppt.	1.00-11.00 yellow; slight brown ppt. 11.00-12.00 light yellow

Table 1. (Cont.)

Metal Ion	Ligand			
	I	II	III	IV
La(III)	No ppt. at any pH	5.50-12.00 white ppt.	No Change	No ppt. at any pH
Pb(II)	No Change	No Change	No Change	No ppt. at any pH
Mn(II)	No Change	5.50-12.00 slight brown ppt.	2.00-4.00 pink 4.50-12.00 yellow; brown ppt.	1.00-5.00 pink 5.00-6.00 red-brown; brown ppt. 6.00-12.00 brown; brown ppt.
Mn(VII)	1.00-5.00 brown ppt. 6.00-11.00 red-brown ppt. 12.00 brown; changes to olive ppt.	5.50-10.00 red 10.00-11.00 red-purple 12.00 purple	1.00-3.00 red-brown 3.00-9.62 brown ppt. 9.62-11.71 clear brown 11.71-12.00 brown ppt.	1.00-6.00 purple 6.00-8.00 brown 8.00-12.00 orange-green
Hg(I)	12.00 slight orange color on standing	5.50-12.00 white ppt.	No Change	1.00-12.00 orange
Mo(VI)	No Change	5.50-12.00 white ppt.	No Change	1.00-12.00 orange
Ni(II)	No ppt. at any pH	5.50-12.00 white ppt.	No ppt. at any pH	No ppt. at any pH
Ni(III)	No Change	5.50-12.00 white ppt.	5.50-12.00 slight white ppt.	No ppt. at any pH
Nb(V)	No Change	5.50-6.90 slight white ppt.	No Change	1.00-8.00 slight white ppt. 8.00-12.00 light orange

Table 1. (Cont.)

Metal Ion	Ligand			
	I	II	III	IV
Pd(II)	1.00-12.00 yellow; lighter at higher pH	No ppt. at any pH	1.00-12.00 slightly yellow	1.00-2.50 yellow-green 2.50-9.50 yellow 9.50-12.00 light green
Re(VII)	No Change	No Change	No Change	7.00-11.00 very light green
Ru(III)	6.00-12.00 brown	5.50-12.00 dark pink	1.00-12.00 light tan	1.00-5.50 brown with purple tinge 5.50-10.00 clear brown 10.00-12.00 yellow brown
Ag(I)	No Change	No ppt. at any pH	1.00-8.00 white ppt.	1.00-12.00 gray ppt.
Sr(II)	No Change	5.50-11.35 white ppt.	No Change	No Change
Te(IV) (TeO ₂ in HCl)	3.90-7.00 slight white ppt.	No Change	No Change	No Change
Tl(III)	No Change	5.50-12.00 brown ppt.	4.00-6.00 pink 6.00-12.00 brown; ppts. on standing	1.00-4.00 purple 4.00-7.00 purple; brown ppt. 7.00-12.00 brown; brown ppt.
Th(IV)	No ppt. at any pH	1.00-9.00 white ppt.	1.00-6.00 slight white ppt.	1.00-6.50 slight yellow ppt. 6.50-12.00 clear yellow
Sn(II)	No Change	No ppt. at any pH	No ppt. at any pH	7.00-12.00 yellow-green

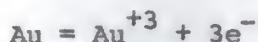
Table 1. (Cont.)

Metal Ion	Ligand			
	I	II	III	IV
Ti(IV)	No Change	5.50-7.00 white ppt.	No Change	1.00-5.00 cloudy yellow-brown 5.00-12.00 cloudy yellow-green
U(VI)	No Change	1.00-7.00 yellow-green ppt. 7.00-12.00 light green	No Change	No Change
V(IV)	No Change	No Change	1.00-2.50 light tan 2.50-4.50 faint pink	1.00-3.00 light orange 3.00-5.00 pink
V(V)	1.00-2.00 light green 3.00-12.00 light yellow	No Change	1.00-3.69 light brown 3.69-4.00 pink 4.00-12.00 colorless	1.00-2.82 orange 2.82-4.28 pink 4.28-5.00 light orange 5.00-12.00 light green
Y(III)	No Change	5.80-12.00 white ppt.	No Change	No Change
Zn(II)	No ppt. at any pH	5.50-12.00 white ppt.	No Change	3.50-4.50 slight white ppt.
Zr(IV)	No Change	No Change	No ppt. at any pH	No ppt. at any pH

1. "No Change" indicates that the solution reacted as if only the metal were present.
2. All numbers refer to pH values.
3. Color designations, unless specified otherwise, refer to the solutions.

anomalous results.

The gold(III)-5-(p-ethoxyanilino)-5,6-dihydrouracil system was chosen because it apparently met the above criteria. The standard oxidation potential of the gold(III) ion, as reported by Latimer (4), is -1.50 volts for the reaction



which indicates that the gold(III) ion is a very powerful oxidizing agent. However, this potential is lowered appreciably by complex formation as its complexes are quite stable. For this reason the oxidizing power of the ion was not a problem.

MATERIALS AND METHODS

The hundredth molar ligand solution used in the final study, 5-(p-ethoxyanilino)-5,6-dihydrouracil, was prepared by weighing 1.2463 g. of the compound on an analytical balance and dissolving it in distilled water to which 10 ml. of concentrated sodium hydroxide solution had been added to make it soluble, then diluting it to 500 ml.

All of the hundredth molar solutions of metal ions were taken from stock solutions which are kept in this laboratory and are composed of reagent grade chemicals dissolved in water, with acid or base added as needed in certain cases to make the substance soluble.

The dioxane used was Mallinckrodt analytical reagent grade. The sodium hydroxide was Fisher reagent grade and perchloric acid was 60 percent reagent grade from Allied Chemical. The

latter two reagents were used to adjust the pH of the solutions to the desired values in the following manner:

A concentrated solution of sodium hydroxide was prepared by dissolving 50 g. of the solid reagent in 50 ml. of distilled water and allowing this to sit, exposed to the air, for several days. At the end of this time a crust had formed on the exposed surface and most of the carbonate left had settled to the bottom of the container, leaving a clear solution of quite pure sodium hydroxide between the two layers. This clear solution was the concentrated sodium hydroxide solution used in these experiments. The perchloric acid was used directly from the bottle.

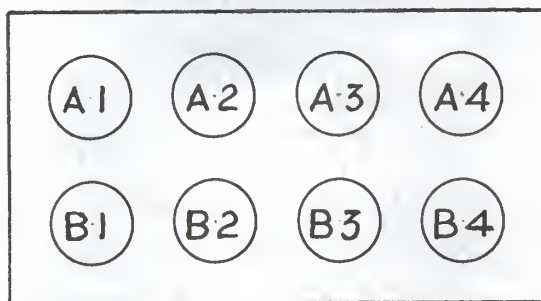


Figure 2. Diagram of the spot plate used for diluting the acid and base.

The concentrated solutions were used to fill two depressions of the spot plate (A1 and B1 of Figure 2). Two drops were taken from each of these solutions with a transfer pipette and placed in adjacent depressions (A2 and B2 of Figure 2), which were then filled with water and thoroughly stirred. After thorough

mixing, two drops were taken to the next depression and the procedure was repeated. After four solutions of both the acid and the base were prepared in this manner, ranging in concentration from concentrated to quite dilute, these were added to test solutions as needed to produce the desired pH by means of a medicine dropper.

A Beckman Zeromatic pH meter was used to determine the pH of the solutions. Mixing was accomplished by means of a magnetic stirrer which was turned off during the actual pH measurement. The electrodes used were a Beckman Model 39170 calomel reference electrode and a Beckman Model 41263 glass indicator electrode.

Spectra and absorption values were obtained with a Beckman Model DB spectrophotometer and Model 93500 recorder. The cells used were matched quartz with a 1 cm. light path.

Determination of Optimum pH and Wavelength

The optimum pH for chelate formation was determined by preparing a solution containing 0.50 ml. of hundredth molar gold(III) and 2.00 ml. of hundredth molar 5-(p-ethoxyanilino)-5,6-dihydrouracil in 25.0 ml. of solution for each of the pH values studied. The pH was adjusted after dilution to values near each pH unit from 1.00 to 12.00. Adjustment of the pH was made by the method described above. The final selection of an optimum pH value was made by varying the pH by 0.10 units in the range which appeared most promising. The spectrum of each solution was recorded and the wavelength which produced the greatest effect was also noted. This pH and wavelength were

then used for subsequent studies.

Continuous Variation Study

A continuous variation study was next undertaken, as described by Job (3) and modified by Vosburgh and Cooper (9). This provided the optimum ratio of ligand to metal and also indicated the composition of the chelate. For this study the total number of moles in the solutions was maintained at a constant value but the ratio of metal to ligand was varied as shown in Table 2.

Table 2. Composition of solutions used in the constant variation study.

Volume Ligand (ml) : Volume Au(III) ml : Mole Fraction Au(III)		
0.50	4.50	0.90
1.00	4.00	0.80
1.50	3.50	0.70
2.00	3.00	0.60
2.50	2.50	0.50
3.00	2.00	0.40
3.50	1.50	0.30
4.00	1.00	0.20
4.50	0.50	0.10

The solutions were diluted to 50.0 ml. after 20.0 ml. of dioxane was added to insure that the chelate would remain in solution. The pH was adjusted to the optimum value after

dilution.

The absorption values obtained at various wavelengths were then plotted versus the mole fraction of gold(III). The maximum or maxima in such a curve indicated the composition of the chelate or chelates formed by this system.

Determination of Analytically Useful Range

Various concentrations of chelate solution were prepared as follows:

<u>Volume Ligand ml.</u>	<u>Volume Au(III) ml.</u>	<u>Concentration Au(III) (Molarity x 10⁴)</u>
10.00	0	0
10.00	0.50	2.00
10.00	1.00	4.00
10.00	1.50	6.00
10.00	2.00	8.00
10.00	2.50	10.00

A mixture of 40 % dioxane and 60% water (by volume) was used to dilute the solutions to 25.0 ml. to give the indicated molarity of Au(III), the pH then being adjusted to the optimum value.

The absorbance of these solutions was determined at the optimum wavelength. From these data it was possible to determine the analytically useful range of this system, and also to determine if it follows Beer's law.

Extraction Studies

Various commonly available organic solvents were tested for their ability to extract the chelate from the aqueous phase. For this purpose the organic solvents to be tested were distilled and only the fraction which boiled at the correct temperature, corrected for atmospheric pressure, was used. The solvents examined were chloroform, toluene, benzene, and a 1:1 mixture of chloroform and toluene. These were the only solvents examined because of a shortage of the ligand solution.

The chelate solution consisted of 1.00 ml. of hundredth molar gold (III) solution, 1.00 ml. of hundredth molar ligand solution and enough water to dilute the solution to 50.0 ml.

The chelate solution and organic solvent were placed in a beaker and the mixture stirred vigorously with a magnetic stirrer under the pH meter. The gas-calomel electrode pair were placed in the aqueous phase and the pH varied from 1.00 to 12.00 to determine the effect of pH on the extractability of the chelate. In cases where the initial test was negative, dioxane was added to the aqueous layer to determine its effect on the extractability.

EXPERIMENTAL RESULTS AND DISCUSSION

Determination of Optimum pH and Wavelength

The optimum pH and wavelength for study of this system was determined by examining the spectra of a number of solutions

differing only in pH. The solutions were composed of 0.50 ml. of hundredth molar gold(III), 2.00 ml. of hundredth molar ligand, and water to produce 25.00 ml. of solution. The pH was then adjusted to the desired value with either sodium hydroxide or perchloric acid.

Figure 3 shows the spectrum of the system at pH 6.20, the optimum value. There was some overlapping of spectra in the different pH ranges. This would indicate that there were various systems in dynamic equilibrium, the amount of a particular species depending on the pH of the solution. From the structure of the ligand this was to be expected, since there are various active sites where coordination might occur or a hydrogen ion might either be added to or removed from the molecule.

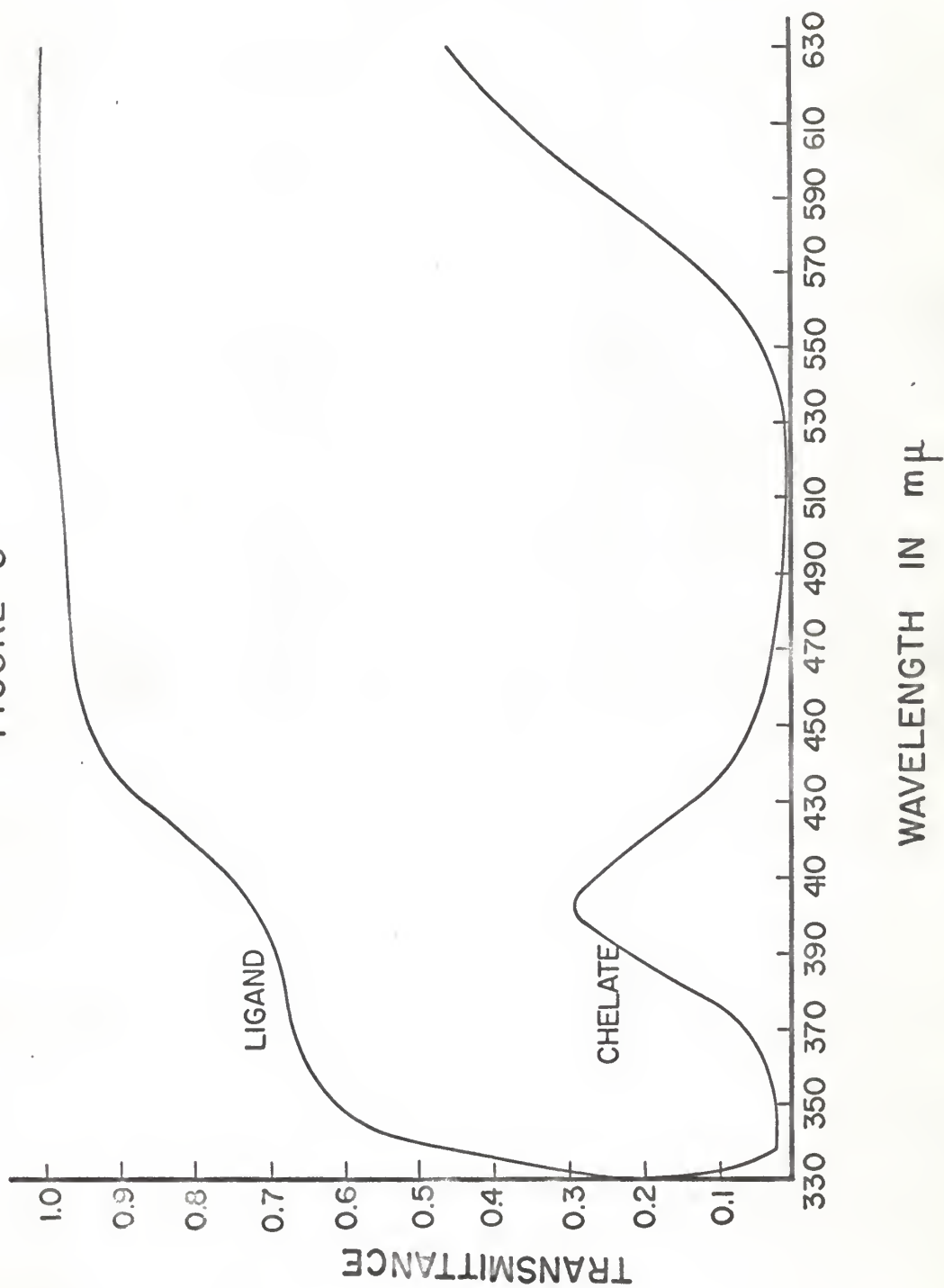
The spectrum of the ligand at the optimum pH value is also included for comparison with the spectrum of the chelate. This solution was of the same composition as the chelate solution except that the metal ion was not added.

From the spectra both the optimum pH for chelation and the optimum wavelength for the study of the chelate are readily determined by the point at which absorbance is a maximum (transmittance is a minimum). The optimum pH was 6.20 and the optimum wavelength was 530 millimicrons.

EXPLANATION OF FIGURE 3

Spectra of the chelate at pH 6.20 from 330 to 630 millimicrons compared with the spectra of the ligand.

FIGURE 3



Continuous Variation Study of the Composition of the Chelate

The method of continuous variation, as developed by Job (3) and modified by Vosburgh and Cooper (9) was used to determine the mole ratio present in the compound or compounds formed by the reactants in this system. The solutions were prepared as indicated under Materials and Methods on page 12. The dioxane added increased solubility of the chelate and did not adversely affect pH measurements in the proportions used, as indicated by Goldberg (2).

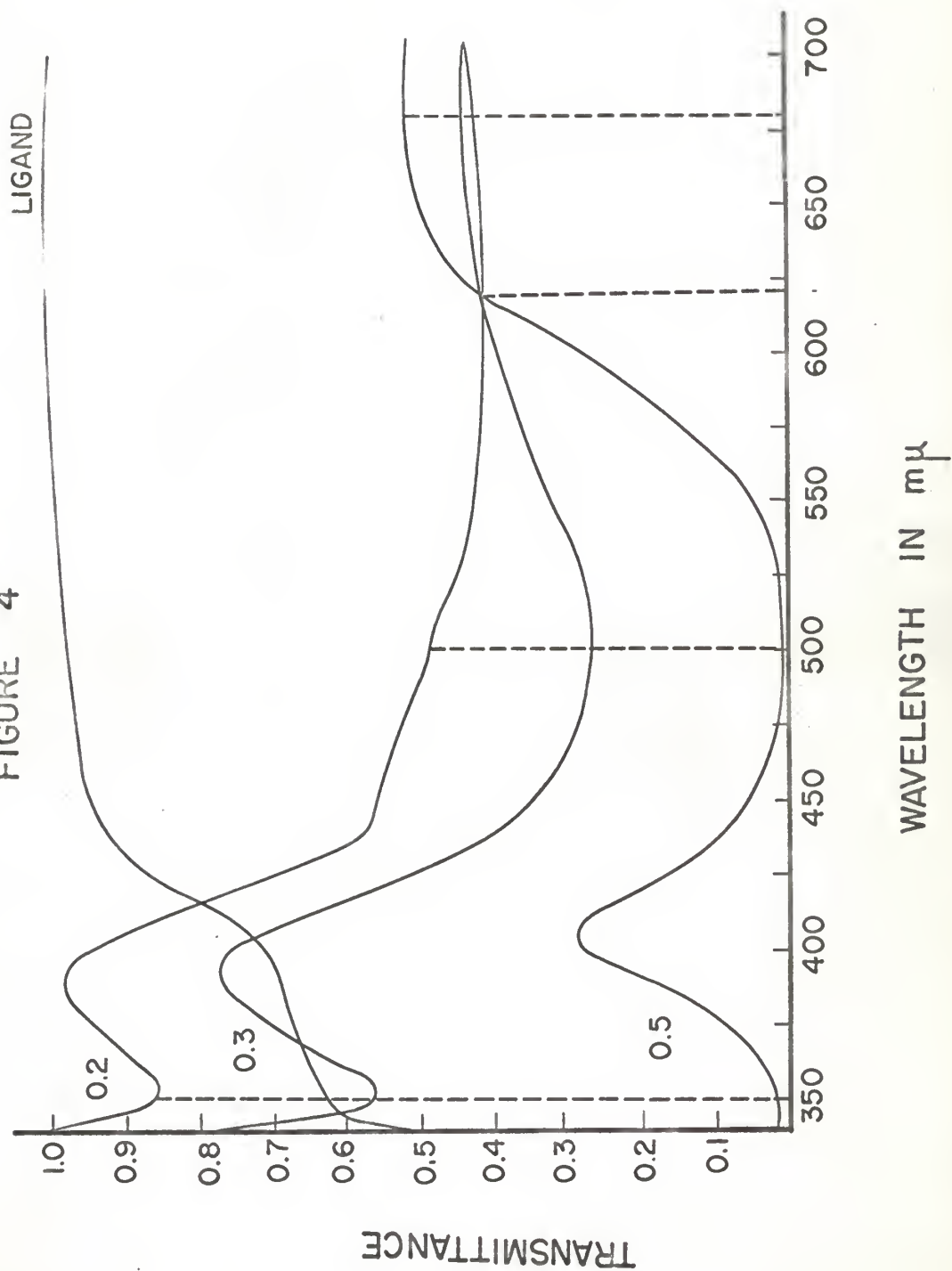
Figure 4 shows the spectra of solutions containing 0.20, 0.30, and 0.50 mole fraction of metal ion and also the spectrum of free ligand at the same dilution. The first two chelate solutions correspond to a metal to ligand ratio of approximately 1:3 and 1:2 respectively, while the third solution has a mole ratio of 1:1. The isosbestic point at 620 millimicrons would indicate that there are at least two compounds formed. This is also borne out by the fact that the shape of the spectra differ, with maxima and minima occurring at different wavelengths. To further confirm this, the absorbance at different wavelengths for the various solutions are plotted on Figures 5, 6, and 7.

The wavelengths chosen for this study were 350 millimicrons, 500 millimicrons, and 680 millimicrons. The first wavelength, 350 millimicrons, was chosen because a minimum occurs here in the spectrum of the 1:1 mole ration solution. The second, 500 millimicrons, was chosen as it is the minimum in the spectrum of

EXPLANATION OF FIGURE 4

Spectra of chelate solutions for the continuous variation study of chelate structure. Solutions containing 0.2, 0.3, and 0.5 mole fraction of Au(III). The first two correspond approximately to a metal to ligand ratio of 1:3 and 1:2 respectively, while the third solution is a 1:1 mole ratio of metal to ligand. The spectrum of the ligand alone is included for comparison.

FIGURE 4



the 1:1 mole ratio solution and the absorption coefficient differs considerably from that for the other two solutions. The reason for selecting 680 millimicrons was that the absorption coefficient for the 1:1 solution is a minimum here and the coefficients for the other two solutions are nearly identical.

Figure 5 shows the absorbance of the various solutions at a wavelength of 500 millimicrons. The height and sharpness of the peak indicates that the compound containing metal and ligand in the ratio of 1:1 is a relatively stable compound which does not dissociate appreciably.

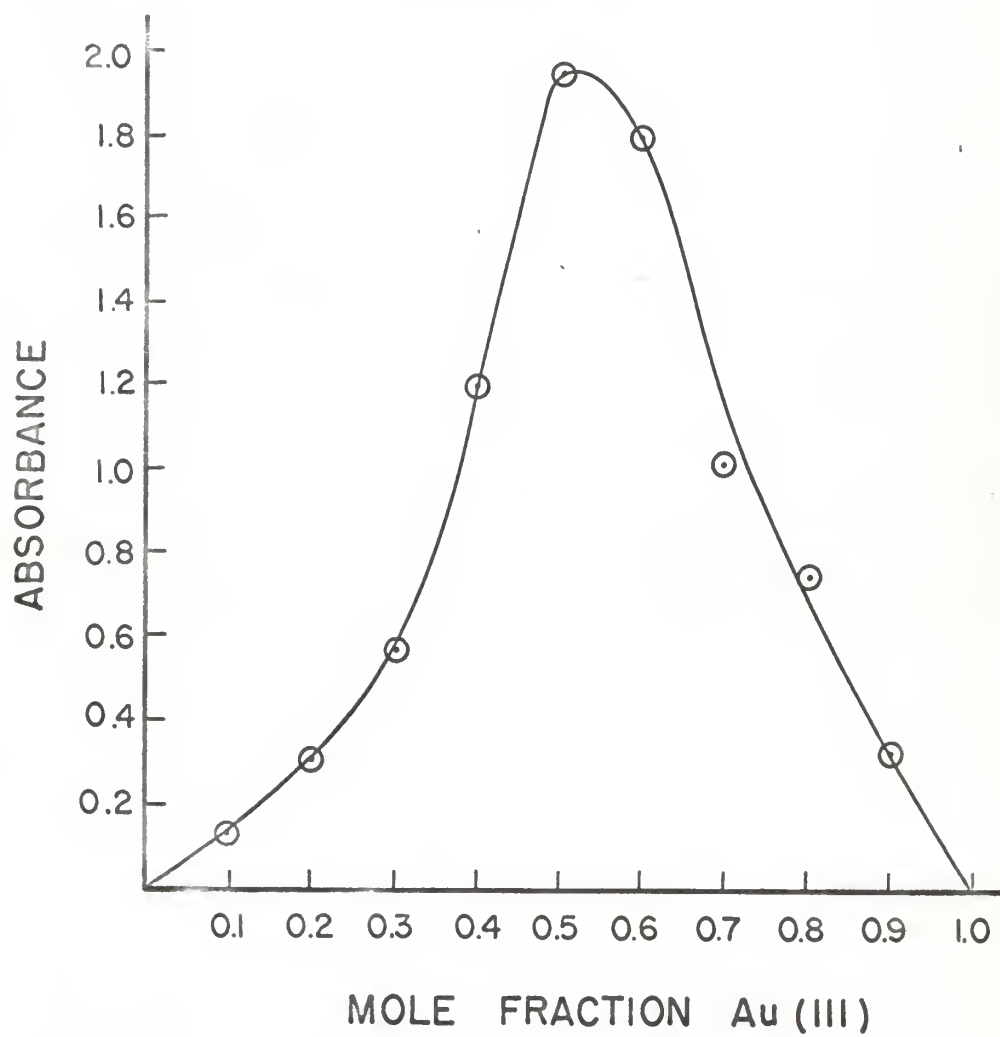
Figure 6 shows the absorbance of the various solutions at 680 millimicrons. This indicates that there are two compounds present rather than just one. The peak at 0.23 mole fraction of gold(III) corresponds very closely to the theoretical peak which would be obtained at 0.25 mole fraction for a metal to ligand ratio of 1:3. The second peak at 0.66 mole fraction of gold(III) is quite close to the theoretically expected peak at 0.67 which would be obtained with a compound in which the ratio of metal to ligand is 2:3. Because these peaks are not as sharp nor as high as the peak obtained for the 1:1 compound, it appears that these compounds are not as strongly bound nor as stable as the 1:1 compound.

Figure 7 shows the absorbance of the various solutions at a wavelength of 350 millimicrons. The maximum value at 0.64 mole fraction of gold(III) corresponds most closely to a theoretical 0.67 mole fraction which would indicate a compound with a metal-

EXPLANATION OF FIGURE 5

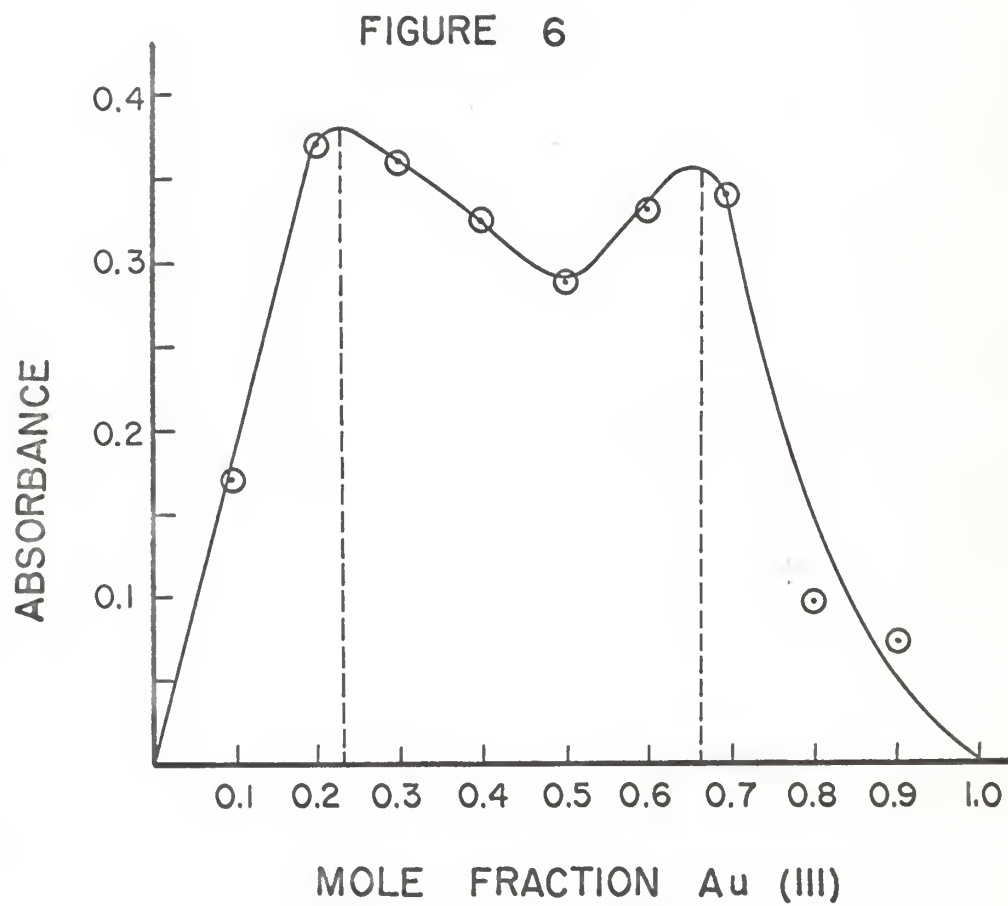
Absorbance of solutions containing various mole fractions of gold(III) at a wavelength of 500 millimicrons.

FIGURE 5



EXPLANATION OF FIGURE 6

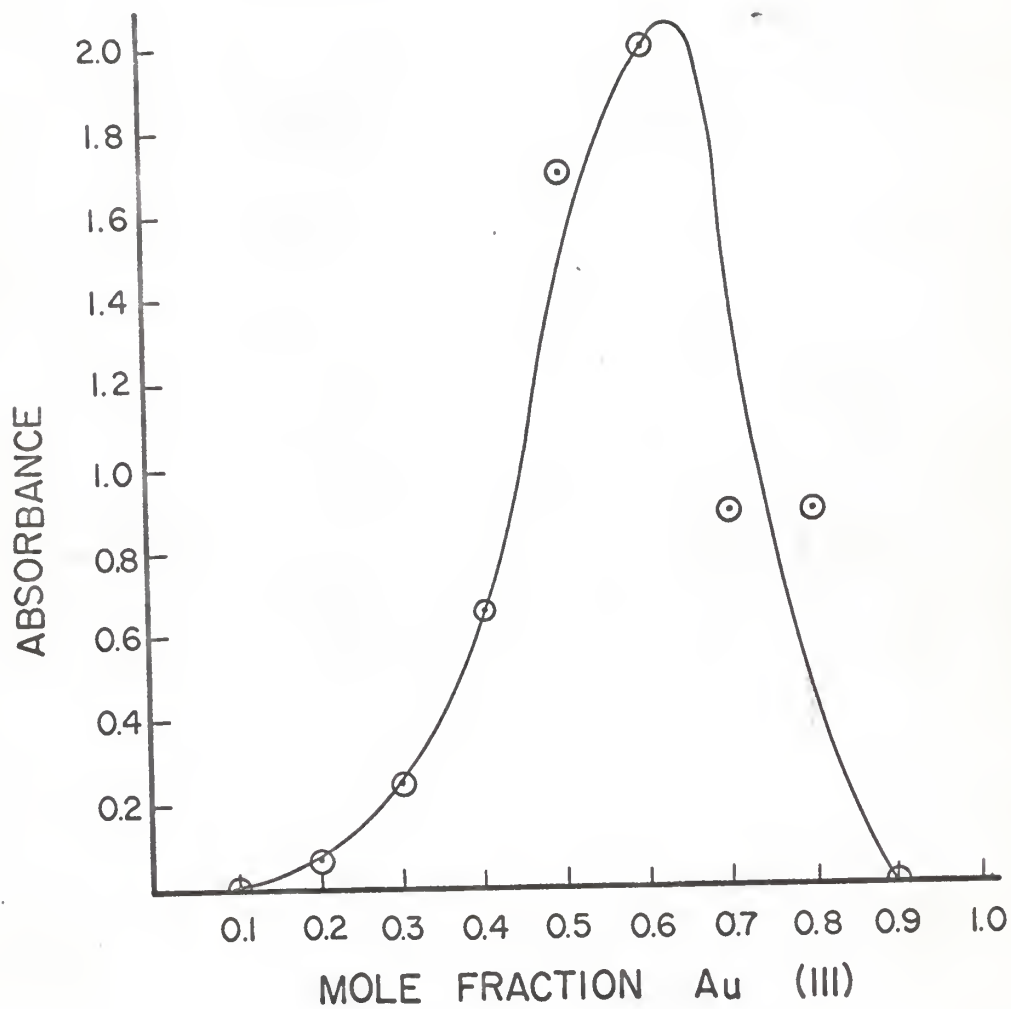
Absorbance of solutions containing various mole fractions of gold(III) at a wavelength of 680 millimicrons.



EXPLANATION OF FIGURE 7

Absorbance of solutions containing various mole fractions of gold(III) at a wavelength of 350 millimicrons.

FIGURE 7



to-ligand ratio of 2:3.

From this data it appears that a series of compounds were formed between gold(III) and 5-(p-ethoxyanilino)-5,6-dihydro-uracil in which the ratio of metal to ligand was first 1:1, then 1:3, and finally 2:3. The most stable compound and the one which predominated at the pH which was used in this study was the middle one in this series, with a mole ratio of 1:1. The others were less stable and had a much lower extinction coefficient which tends to indicate that they dissociated much more completely at this pH than the 1:1 compound. However they were present in sufficient quantity to be analytically significant. They tended to cause this system to deviate from Beer's law, but by construction of a calibration curve they will cause no difficulty in applying this system analytically.

Determination of Analytically Useful Range

This experiment not only provided the data for determination of the useful analytical range of this system, but also indicated the degree to which this system follows Beer's law. In the last section it was indicated that this system probably would not follow Beer's law too exactly as there are three competing species in equilibrium. For this experiment to be valid, the amount of ligand must remain constant as it would in an actual analytical determination. Therefore, as the concentration of metal was varied, the ratio of metal to ligand was varied also, tending to favor the different compounds as the stoichiometric

ratio favorable for each compound was reached. As the extinction coefficient for each compound is different, this will cause the absorption of light to vary from the value which would be theoretically calculated for any one of the compounds using Beer's law.

Figure 8 is the graph of the following data obtained in this experiment.

Table 3. Absorbance of solutions containing 10.0 ml. of ligand and various concentrations of Au(III) in 25.0 ml. of solution.

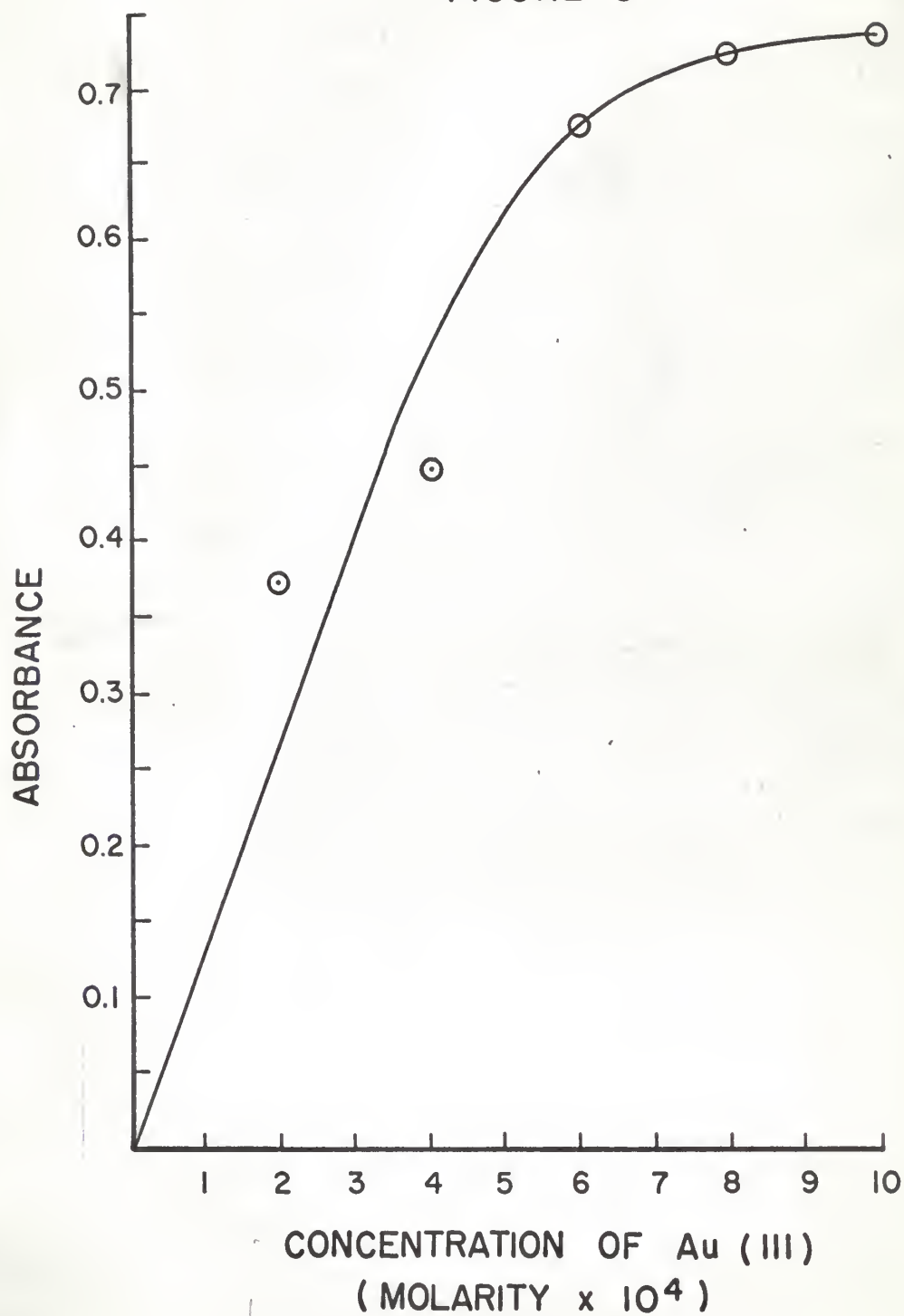
Concentration of Au(III) (Molarity $\times 10^4$)	:	Absorbance
2.00	:	0.373
4.00	:	0.448
6.00	:	0.676
8.00	:	0.721
10.00	:	0.733

The absorbance of these solutions did not follow Beer's law as is indicated by the curved rather than straight line on Figure 8. However, the system is analytically useful in the range of concentrations tested. Beyond this range precipitation occurs when the solution was prepared. The last three solutions also precipitated upon standing for 5 minutes. For this reason solutions should be photometrically examined within 5 minutes of the time they are prepared.

EXPLANATION OF FIGURE 8

Beer's law curve showing the absorbance of solutions containing various concentrations of gold(III) up to the analytically useful limit of this system.

FIGURE 8



Interfering Ions

In the course of this investigation cations which did not interfere with the system when present in the same concentration as the gold(III) ion were La(III), Li(I), Mo(VI), NH_4 (I), K(I), Na(I), Ti(IV), U(VI), and V(V). Anions which met this same criteria were the nitrate, chloride, acetate, and oxalate ions. Cations which produce a color or precipitate with the ligand, therefore interfering with this system were Sb(V), Ce(IV), Cr(VI), Co(II), Co(III), Cu(I), Cu(II), Ir(IV), Fe(II), Fe(III), Mn(II), Mn(VII), Hg(I), Nb(V), Pd(II), Re(VII), Ru(III), Ag(I), Tl(III), Th(IV), Sn(II), Ti(IV), V(IV), and Zn(II).

Determination of Extractability

It is frequently advisable to extract a chelate from the aqueous phase into an organic phase due to the low solubility observed in water. For this reason various common organic solvents were investigated as extractants for the gold(III)-5-(p-ethoxyanilino)-5,6-dihydrouracil system investigated here.

Benzene did not extract the chelate at any pH. Chloroform was somewhat effective at pH values greater than 5.00, but was not too effective at any pH. Toluene extracted the chelate slightly below a pH of 6.00, but it was not quantitative at any pH.

A mixture of chloroform and toluene in the ratio of 1:1 (by volume) was the most effective extractant. The optimum pH for extraction was between the values of 6.00 and 6.50. Extracta-

bility was enhanced by the addition of sodium hydroxide to the aqueous layer. However, the extraction still was not quantitative.

Bjerrum Titration

A Bjerrum titration was attempted, but was unsuccessful due to the presence of several compounds in equilibrium. The only information gleaned from the titration was the pK_a of the acid, which was 4.32. This gives an acid ionization constant for the ligand of 4.8×10^{-5} .

RECOMMENDED ANALYTICAL PROCEDURE

In order to analyze a sample for gold by this method, the gold must first be converted to the +3 oxidation state. This may be done most conveniently by dissolving a solid sample in aqua regia.

A solid sample of about 2.0 grams should be treated with 25 ml. of aqua regia for one-half hour, then boiled until nearly dry to expel excess acid. The residue should then be taken up in approximately 50 ml. of water and filtered to remove residual solids.

The resulting clear solution should then be placed in a 250 ml. volumetric flask and 20.0 ml. of hundredth molar 5-(p-ethoxy-anilino)-5,6-dihydrouracil solution added and the solution diluted to the mark with a sodium oxalate-oxalic acid buffer solution of pH 6.20.

After thorough mixing the test solution should be examined at a wavelength of 530 millimicrons within five minutes after mixing. The concentration of gold(III) is then determined by comparison with a calibration graph prepared from a series of standard solutions containing gold in the form of HAuCl_4 .

SUMMARY

In the first phase of this thesis the optimum pH for the formation of a chelate between gold(III) and 5-(p-ethoxyanilino)-5,6-dihydrouracil was found to be 6.20. The wavelength at which its extinction coefficient was a maximum was found to be 530 millimicrons. The pK_a of the ligand was determined to be 4.32.

A continuous variation study as described by Job (3) and modified by Vosburgh and Cooper (9) was next utilized to determine the number and composition of chelates formed by this system. Compounds were found with metal to ligand ratios of 1:1, 1:3, and 2:3. The predominant one at a pH of 6.20 is the 1:1 compound, the others are less stable and have a lower extinction coefficient.

The system was next found to be analytically useful for concentrations of gold(III) between 4.00×10^{-5} and 10.00×10^{-4} molar. The useful range was extended by using a mixed solvent of 40 percent dioxane and 60 percent water, by volume. The system did not follow Beer's law exactly, as would be expected of a system containing three compounds in equilibrium.

Cations which did not interfere with the system were La(III) ,

Li(I) , Mo(VI) , $\text{NH}_4\text{(I)}$, K(I) , Na(I) , Tl(IV) , U(VI) , and V(V) .

Anions which were found to be non-interfering were the nitrate, chloride, acetate, and oxalate ions. Cations which produced a color or precipitate with the ligand and would thus interfere with this system were Sb(V) , Ce(IV) , Cr(VI) , Co(II) , Co(III) , Cu(I) , Cu(II) , Ir(IV) , Fe(II) , Fe(III) , Mn(II) , Mn(VII) , Hg(I) , Nb(V) , Pb(II) , Re(VII) , Ru(III) , Ag(I) , Tl(III) , Th(IV) , Sn(II) , Ti(IV) , V(IV) , and Zn(II) .

The extractability of the chelate with organic solvents was investigated. A 1:1 mixture (by volume) of chloroform and toluene was found to extract the chelate between a pH of 6.00 and 6.50 if 5.00 ml. of concentrated (50 percent by weight) sodium hydroxide was present in 50.0 ml. of chelate solution. The extraction was not quantitative however. Other solvents investigated were benzene, chloroform, and toluene.

A recommended analytical procedure is also outlined.

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A SPECTROPHOTOMETRIC STUDY OF THE
GOLD(III)-5-(p-ETHOXYANILINO)-5,6-DIHYDROURACIL CHELATE

by

DELBERT ALLAN MARSHALL

B. S., Kansas State Teachers College of Emporia, 1959

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The Au(III)-5-(p-ethoxyanilino)-5,6-dihydrouracil system was studied spectrophotometrically to determine its chemical characteristics. The optimum pH for the system was found to be 6.20 and the optimum wavelength for its study was found to be 530 millimicrons. The pKa of the ligand was determined by titration with sodium hydroxide to be 4.32, corresponding to an acid ionization constant of 4.8×10^{-5} .

Compounds with metal-to-ligand ratios of 1:1, 1:3, and 2:3 were indicated by Job's method of continuous variation as modified by Vosburgh and Cooper. Absorption maxima for these compounds were found at 500 millimicrons, 680 millimicrons, and 350 millimicrons respectively, at a pH of 6.20. The 1:1 compound predominates at this pH and 530 millimicrons.

The system was found to have an analytically useful range to a molar concentration of 10.0×10^{-4} for Au(III). The minimum concentration of Au(III) that it was possible to detect was 4.00×10^{-5} molar.

Cations which were shown to be non-interfering with the chelate were La(III), Li(I), Mo(VI), NH_4 (I), K(I), Na(I), Ti(IV), U(VI), and V(V). Anions which did not interfere with the chelate were the nitrate, chloride, acetate, and oxalate ions. Cations which interfere with this system (those which produce a color or precipitate with the ligand) were Sb(V), Ce(IV), Cr(VI), Co(II), Co(III), Cu(I), Cu(II), Ir(IV), Fe(II), Fe(III), Mn(II), Mn(VII), Hg(I), Nb(V), Pd(II), Re(VII), Ru(III), Ag(I), Tl(III), Th(IV), Sn(II), Ti(IV), V(IV), and Zn(II).

The extractability of the chelate with organic solvents was investigated. Chloroform, benzene, and toluene did not extract the chelate appreciably at any pH. A 1:1 mixture (by volume) of chloroform and toluene was found to extract the chelate at pH values between 6.00 and 6.50 in the presence of sodium hydroxide, although the extraction was not quantitative.

This Au(III)-5-(p-ethoxyanilino)-5,6-dihydrouracil system would be analytically useful for the determination of Au(III) in the range of 4.00×10^{-5} to 10.00×10^{-4} molar. Because there are three different compounds in equilibrium the system would not be suitable for gravimetric determinations.